New Developments in Glass Contact Refractory Channel Blocks

The purpose of this paper is to describe the development of a new refractory material specifically for use as forehearth channel blocks. However in order to establish a benchmark for comparison it is necessary to review the various materials that are currently in use. The following therefore are the major types of forehearth channel block materials past and present. This list includes only those materials used for mainstream glass production, principally soda-lime-silica glasses, and ignores those used in speciality applications.

- Sillimanite normally slip cast with a 55-65% Al₂O₃ content.
- Mullite normally slip cast with a 65-70% Al₂O₃ content.
- Zircon-mullite normally slip cast with a 70-75% Al₂O₃ and a 10-15% ZrO₂ content. Some chemically bonded zircon-mullite channels are also manufactured.
- High alumina normally slip cast with a 90-93% Al₂O₃ content.
- Fused cast AZS normally with a 32% ZrO₂ content.
- Fused cast α - β alumina normally with a 95% Al₂O₃ content.

All these types of channel material have different attributes which I would summarise as follows.

Sillimanite channel blocks

Sillimanite is a generic name for refractory materials containing 55-60% Al₂O₃. Since commercial extraction of the natural sillimanite mineral ceased around 1970 however alternative minerals such as andalusite, kyanite, or synthetic equivalents, have been used.

Sillimanite channel blocks were popular up to 20-30 years ago when furnace campaigns were planned for 5-6 years. However as campaign lives and forehearth tonnages have increased this type of channel block has largely been phased out. Being a sillimanite product however it was competitively priced. PSR discontinued the manufacture of sillimanite channel blocks some years ago.

Mullite channel blocks

Mullite takes its name from the Isle of Mull in Scotland, the only known naturally occurring source, although it has never been available in sufficient quantities for commercial exploitation. Mullite refractories are therefore manufactured from synthetic materials, produced either as sintered mullite or fused mullite. Being made synthetically mullite grains have a higher purity and a higher refractoriness than the sillimanite type materials and can therefore be expected to have a longer service life.

High alumina channel blocks

High alumina channel blocks are made from a blend of aluminous minerals such as tabular alumina, hydrated alumina and mullite in order to arrive at an Al₂O₃ content above 90%. Again, in terms of purity and refractoriness they could be expected to outperform the mullite type of channel block.

Zircon mullite channel blocks

Zircon mullite channel blocks can be divided into two types.

- The first type is that made directly from the constituent minerals of zirconium-silicate, alumina and mullite. The refractory bonding takes place in the firing process at high temperatures as the zirconium-silicate dissociates to zirconia and silica, and the silica reacts with the alumina to form mullite. The composition '333', as produced by PSR and other Emhart licensees, is manufactured by this process and has been the principal bonded refractory channel block in use for the past 20-25 years.
- 2. The second type is that made from synthetic materials, usually fused zirconia-mullite or zirconalumina. This type of refractory is formed by a process commonly referred to as 'chemical bonding' and involves the addition of reactive silica to encourage the formation of mullite. This type of refractory material is popular outside the glass industry, and has found favour with glass in noncontact applications, but has not proved as successful in glass contact applications.

Fused cast AZS channel blocks

Fused cast AZS channel blocks are composed of alumina, zirconia and silica, and normally contain a minimum of 32% ZrO₂. In the furnace melting end fused cast AZS furnace blocks are highly resistant to corrosion. At the lower temperatures in the forehearth however their resistance to corrosion is much less than would be expected. Furthermore, with around 20% glassy phase, of which as much as 3% can be exuded on heat-up, their application in the forehearth is generally limited to particularly aggressive glasses or high temperature forehearths where no other material is suitable.

Fused cast α-β alumina channel blocks

Fused cast α - β alumina channel blocks generally contain around 95% alumina. At temperatures above 1370°C their corrosion resistance is inferior to that of fused cast AZS but at typical forehearth temperatures they are the most corrosion resistant of the channel blocks described here. Fused cast α - β alumina channel blocks are favoured because of their low glassy phase (typically 2%), their lack of exudation on heat-up, their low stoning and blistering counts, and their good resistance to corrosion. From a commercial perspective however they are generally the most expensive option of any listed above by a considerable margin.

Comparative corrosion resistance

The following graph represents an estimate of corrosion resistance for various channel materials in a typical soda-lime glass forehearth. Typical temperatures have been assumed to be 1250°C entry temperature and 1125°C gob temperature.





Comparative costs

Cost would not normally be a feature of a technical paper but it is a significant influence over the selection of channel block refractory materials. My estimate of relative costs for current materials is represented by the following chart, where fused cast α - β alumina is the most expensive at index 100.



Estimated comparative costs of channel block materials

Development of a New material

Based upon our experience with installing 333 channel blocks over the past 25 years we believe that PSR-333 can easily accommodate the current 10+ year life expectancy of most container glass forehearths. Its lack of glassy phase, low zirconia content and low corrosion rate also make it an unlikely source of zircon or alumina related cat-scratch cord.

Nevertheless there remain a significant number of glassmakers who prefer to use fused cast α - β alumina, partly because of its purity and absence of zirconia, and partly because of its resistance to corrosion.

In 1999 therefore we embarked on a research programme to develop a new bonded refractory material containing no zirconia and with a glass corrosion index equivalent to fused cast α - β alumina. This research was carried out in partnership with Leeds University as part of the UK Government's 'Teaching Company Scheme'.

Initial Work.

We began the project by characterising PSR 333 – a known material with excellent corrosion resistance. We first wanted to establish which of its properties really contributed to its corrosion resistance.

Was it only the low solubility of Zircon?

Microscopy and X-ray diffraction studies indicated that the low solubility of zircon was relevant but that the major roll was its decomposition at the glass-refractory interface, giving a low porosity zirconia-rich barrier layer approximately 2mm thick at the glass contact surface.

This dense barrier layer, developed due to the volume changes associated with the decomposition of zircon to zirconia and the transformation of zirconia from the monoclinic to tetragonal form, prevents the ingress of glass, thus limiting the surface area available for corrosion to take place.

In order to examine the effect of zircon further we trialled different compositions with different amounts of zircon and we found that greater amounts did not necessarily enhance corrosion resistance. In fact compositions with minimal amounts of zircon could be found to have corrosion resistance equivalent to the standard 333 formulation.



Photograph showing the dense zirconia-rich barrier layer found in PSR-333.

The presence of zircon as such therefore was not the biggest influence on corrosion. However, if we were to remove the zircon completely some other way would have to be found to provide a dense glass corrosion barrier and we identified porosity and pore size distribution as being the key areas for investigation. In initial tests, for corrosion resistance equivalent to 333, we found that a reduction in porosity from ~22% to ~16% compensated for the removal of zircon. We therefore set ourselves a target porosity of 10-12% for a non-zircon containing product.

Particle packing

In simple terms particle packing is the optimisation of spheres packed into a given volume to obtain the highest density. Mathematical modelling techniques developed by Andreasen in the 1930's and by Funk and Dinger in the 1970's can simulate this problem and we used predictive software developed by Ceram Research to accelerate the results. Looked at simplistically one might think that a fine powder would leave the least gaps and therefore have the highest packing density but that ignores the need to use different particle sizes and different aggregates to obtain the ideal ceramic system. Multiple regression analysis is required to determine the relative proportions of all these different sized grains in a perfectly packed system and although grains are irregular in shape it does provide an accurate guide to optimising the density of refractory formulations.

Laboratory mixes based upon the calculated particle packing results achieved the required densities but were disappointing in their corrosion characteristics and we identified this as being due to the presence of mullite. This acted as a barrier to sintering and gave a pore size which allowed penetration of glass into the interior structure, a defensive roll undertaken by the zircon in PSR 333 material.

The decision was therefore taken to remove mullite from the formulation and replace it with alumina to achieve a single-phase material with a high capacity for sintering. Further regression analysis was carried out and the new material formulated. Fired results were encouraging with porosities of 15-16% being consistently achieved and glass corrosion results were equivalent to the standard PSR 333 as predicted.

However in order to match the corrosion resistance of fused cast α - β alumina a further and significant reduction in porosity would be necessary.

The Final Formulation.

In order to achieve lower porosities the range of particle sizes was extended to the micron range and further regression analysis carried out on the fine fractions to optimise the mix. There is a limit to the extent to which this approach can be taken since the production of large pieces by slip casting requires a degree of porosity to allow the removal of moisture. Porosities of 9.5% however were consistently achieved in the laboratory and at this stage we commenced factory production trials.

Production.

In order to achieve the elevated firing temperatures necessary for extreme sintering two small factory kilns were converted to higher temperature firing and a third new high temperature kiln is due for delivery at the end of 2004. Production in the factory also required some modifications to mixing and casting techniques and average porosity increased slightly compared to laboratory production. However, porosity values of 12% were achieved consistently so samples were taken and submitted to NAMAS accredited laboratories for full testing.

Results

phase.

Chemical & physical properties

The new material is known as PSR-993 and its chemical and physical properties are as follows.

	<u>PSR-333</u>	Fused cast	<u>PSR-993</u>
	<u>(zircon-mullite)</u>	<u>α-β alumina</u>	<u>(dense bonded</u>
		(typical values)	<u>alumina)</u>
Al ₂ O ₃	73%	95%	99.7%
SiO ₂	15%	0.5%	nil
ZrO ₂	11.1%	nil	nil
Vitreous phase	nil	2%	nil
Bulk Density	2820 kg m ⁻³	3170 kg m ⁻³	3400 kg m ⁻³
Cold crushing strength	87.3 M Pa	200 M Pa	474 M Pa
Apparent solid density	3650 kg m ⁻³	3540 kg m ⁻³	3750 kg m ⁻³
Apparent Porosity	21%	1.6%	11%



Corrosion resistance

Samples of PSR-333, fused cast α - β alumina and the new material PSR-993 were submitted to Glass Technology Services and subjected to a static corrosion test in soda lime glass for 72 hours at 1370°C. PSR-333 recorded 13% corrosion, fused cast α - β alumina 8.6% and PSR-993 7.7%. A graph of the percentage corrosion and the photograph of the samples are reproduced below.

(The marking on the fused cast α - β alumina sample has been covered to protect the manufacturer's identity.)





PSR-993 recorded the least corrosion.



Photograph of static corrosion test of (from left to right) PSR-333, the new material PSR-993 and fused cast α - β alumina.

PSR-993 (centre) exhibits the least corrosion.

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Electrical resistivity

For electrically heated forehearths, or those forehearths with supplementary electrical heating for trim control, electrical resistivity is an important attribute. Samples of the new material were tested by Ceram Research and the results are plotted below. The electrical resistivity of PSR-993 is approximately 10 times that of fused cast α - β alumina.



Electrical resistivity of PSR-993

Thermal conductivity

With a high density and low porosity PSR-993 is more conductive than PSR-333 but at normal forehearth operating temperatures is significantly less conductive than fused cast α - β alumina. This should be a significant factor in reducing attack at the channel joints that is a feature of the corrosion pattern with fused cast α - β alumina channel blocks.

The results as tested by Ceram Research are plotted below.



Thermal conductivity of PSR-993

Thermal expansion

Thermal expansion is linear and the results as tested by Ceram Research are plotted below. Permanent Linear Change (PLC) is zero.



Linear expansion of PSR-993



Bubble & stone tests

Tests for bubble & stone are extremely subjective and reference to published data reveals indices that vary widely in their definition. We submitted samples of 993 and 333 to Glass Technology Services for comparison against standard fused cast α - β alumina samples. Their comments were as follows. *"993 looks to be comparable to the fused cast* α - β *alumina sample and better than 333. There are a few sub 1mm bubbles, but no bubbles at the base of the sample itself. The glass colour is also good. The GTS value for this would be 6, just slightly better than the fused cast* α - β *alumina sample."*



Cross-section of bubble & stone test samples of fused cast α - β alumina (left) and PSR-993 (right). Each sample had a 20mm \emptyset hole filled with soda lime glass at 1370 % for 72 hours.

Conclusion